Rhodium complexes bearing tetradeutate diamine-bis(phenolate) ligands†

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Using tetradeutate, dianionic ligands, several new rhodium complexes have been prepared. Some of these diamine-bis(phenolate) compounds, are active for C–H activation of benzene. These complexes are air and thermally stable. All four complexes were characterized by X-ray diffraction.

Introduction

First reported in 2000,† the family of trans-(κ²-acac-O,O)Ir(R)(L) (acac = acetylacetone, R = hydrocarbyl, L = dative ligand) O-donor complexes have been shown to be capable of activating C–H bonds and catalyze the selective, anti-Markovnikov hydroarylation of unactivated olefins with arenes.‡ These complexes are relatively simple to synthesize and remarkably, likely due to unique properties imparted by O-donor ligands, solutions are thermally stable to air and basic as well as acidic media. Mechanistic studies show that these trans bis-acac-O,O Ir(III) complexes are catalyst precursors and that the active catalysts are generated by loss of L, followed by rate determining trans to cis isomerization to generate coordinatively unsaturated, five-coordinate pseudo square pyramidal complexes with the four O's of the two acacO,O ligands in a meridional geometry that places the R group cis to an open site.† In an effort to design more active catalysts with similar reactivity and stability we sought to explore related metal complexes towards arenes.

Results and discussion

The ligands H₂N=N’N’O₂ (1a), H₂NMe₂=N’O₂Me (1b), and H₂NN’O₂Me (1c) were synthesized in a single-step Mannich condensation reaction using the general procedure developed by Kol and coworkers. The reaction of H₂NN’O₂ ligands with the commercially available RhCl₃·(H₂O), afforded the chloro complexes 2a, 2b, 2c as yellow-orange microcrystalline solids in moderate yields as shown in Fig. 1. These complexes were readily crystallized from a mixture of CH₃OH–CHCl₃ (1:1) at –30 °C, which were then analyzed by X-ray crystallography (see supporting information for the metric parameters for complexes 2a–2c†). The geometry around the Rh center for all three complexes can be described as a distorted octahedral and the ORTEP drawing of the molecular structures of 2a, 2b, and 2c are presented in Fig. 2. As can be seen the tetradeutate NN’O₂ spectator ligands enforce a meridional geometry in these complexes that afford the...
required cis-geometry for the other two sites where reaction could occur. The structures for 2a, 2b, and 2c in the solid state are consistent with solution NMR data with a trans-O,O for 2a, with trans-O,O for 2b, with trans-bond angles O(1)–Rh(1)–O(2), O(3)–Rh(1)–N(1), and Cl(1)–Rh(1)–N(2) of 176.08(9), 174.89(11), and 178.26(8) respectively, trans-O,O for 2b, with trans-bond angles O(1)–Rh(1)–O(2), O(3)–Rh(1)–N(1), and Cl(1)–Rh(1)–N(2) of 170.68(13), 176.73(14), and 178.75(13) respectively, and cis-O,O for 2c with trans-bond angles O(1)–Rh(1)–Cl(1), O(3)–Rh(1)–N(2), and O(2)–Rh(1)–N(1) of 174.26(17), 177.1(2), and 175.4(2) respectively.

The selective trans-O,O in 2a and cis-O,O in 2c may be attributed to the subtle steric bulk between the two tert-butyl substituents in 2a. Similar selectivity in geometry is consistent with the observations made by Mountford and coworkers for the corresponding Zr(NpyN(NO)Cl), [trans-O,O], and Zr(NpyN(NO)Cl), [cis-O,O]. However, it is not a priori obvious why complex 2b also favors trans-O,O. Consequently, we turned to DFT calculations (B3LYP/LACVP** using Jaguar 6.5 program suite, see supporting information†). DFT calculations on the complexes cis/trans-2a indicate that the trans-2a (0.0 kcal mol$^{-1}$) is favored over cis-2a (3.4 kcal mol$^{-1}$). Similarly, trans-2b (0.0 kcal mol$^{-1}$) is favored over cis-2b (2.8 kcal mol$^{-1}$) and cis-2c (0.0 kcal mol$^{-1}$) is favored over trans-2c (1.5 kcal mol$^{-1}$). Since the cis-trans isomers are only separated by a couple kcal mol$^{-1}$ in solution, if the barrier to rearrange is manageable, both would be accessible during catalysis.

Moreover, as expected, the calculations suggest that the methyl analogues 2b and 2c do not show any preferences on the basis of steric in either cis or trans-O,O coordination. However, trans-2c exhibits substantial angle strain in the Rh–N–CH$_2$–C$\equiv$N–Rh metallacycle, as the coordination of the two phenolates trans to each other “push” the metallacycle into a planar configuration. This is not a problem in trans-2b, with a more flexible side arm as compared to complex 2c.

Thus, we can conclude that electronically, the trans-O,O coordination is favored by 3 kcal mol$^{-1}$. Making the N–C–C–N bridge more rigid increases the energy of the trans-O,O coordination, causing cis-2c to be favored, while the introduction of steric on the phenolates increases the energy of the cis-O,O coordination, thus favoring the trans-O,O coordination in 2a.

The Rh–N(1) distances vary from 2.019(7) to 2.040(2) Å in this set of compounds. While, the Rh–N(2) distances vary over much of this range for this series, 1.958(6) to 2.095(4) Å. In addition, the Rh–O distances vary together and are the same within error in complexes 2a–2c. The Rh–Cl distances are particularly sensitive to changes in ligands on Rh and, vary from 2.3475(13) to 2.3757(9) Å.

We were particularly interested in preparing Rh–Ar derivatives because of their importance as catalysts for C–H activation. Consequently, reaction of 2c with Ph$_2$Hg in CH$_2$Cl$_2$–CH$_3$OH (2:1) at room temperature afforded complex 3 as a yellow-orange powder in 60% yield. PhLi, Ph$_2$Zn and PhMgBr afforded complex reaction mixtures. Crystallization from CH$_2$Cl$_2$–hexane (1:1) yielded microcrystals of 3, which were analyzed by X-ray crystallography. The ORTEP drawing of the molecular structure of 3 is presented in Fig. 3. The solution NMR data and the solid state structure for 3 closely resembles 2c, with the only notable difference being the expected replacement of the chloride with a phenyl group. The trans-bond angles O(1)–Rh(1)–N(2), O(2)–Rh(1)–C(25), and O(3)–Rh(1)–N(1) are 175.6(3), 173.2(3), and 177.2(3) respectively. The Rh(1)–C(25)
Table 1  Comparison of the bond lengths (Å) of different Rh(III)–C(phenyl) bonds in the crystal structures of 3 and analogous complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Rh–C(phenyl)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh(N=N=O2=O)(CH3OH)(Ph) (3)</td>
<td>2.037(9)</td>
<td>This work</td>
</tr>
<tr>
<td>Rh(acac-O)=O(=CH3)(CH3OH)(Ph)</td>
<td>1.970(3)</td>
<td>8</td>
</tr>
<tr>
<td>Rh(PNp)Ph(=Br)</td>
<td>2.005(6)</td>
<td>9</td>
</tr>
<tr>
<td>RhCp*(O)(=CH2)SiMe3)(PMc)(Ph)(=Br)</td>
<td>2.0636(12)</td>
<td>10</td>
</tr>
<tr>
<td>RhCp*(=Pm)(Ph)(Br)</td>
<td>2.054(9)</td>
<td>11</td>
</tr>
<tr>
<td>RhCp*(PMc=Ph)(Ph)(Br)</td>
<td>2.082(6)</td>
<td>12</td>
</tr>
<tr>
<td>RhCp*(PMcPh)(Ph)(Br)</td>
<td>2.065(5)</td>
<td>12</td>
</tr>
<tr>
<td>RhCp*(PhH)(Ph)(Br)</td>
<td>2.081(1)</td>
<td>12</td>
</tr>
<tr>
<td>[RhCp*(PMe3)(Ph)(CH2Cl2)][BAr]F4</td>
<td>2.026(8)</td>
<td>13</td>
</tr>
</tbody>
</table>

In summary we have reported a series of Rh(NNMe2N¢O2=O)(=Cl)(CH3OH) (2a). A 50 mL Schlenk bomb was loaded with RhCl3·(H2O)3 (230 mg, 0.89 mmol) in water (5 mL). To this was added a solution of H2NpyN¢O2=O (485 mg, 0.89 mmol, 1 equiv.) in acetone (10 mL). The reaction mixture was heated at 80 °C for 5 min to afford a homogeneous orange solution. After 5 min, NaHCO3 (150 mg, 1.78 mmol) was added to the reaction mixture and the mixture heated at 80 °C for 220 °C under dynamic vacuum for at least 24 h, then stored under argon. RhCl3·(H2O)3 was purchased from Pressure Chemical Co. and used without purification. All high-resolution mass spectra were obtained by UCLA Pasarow Mass Spectrometry Laboratory on either an ESI or a MALDI-TOF mass spectrometer.

Synthesis of Rh(N=N=O2=O)(=Cl)(CH3OH) (2a). A 50 mL Schlenk bomb was loaded with RhCl3·(H2O)3 (230 mg, 0.89 mmol) and purified through alumina columns to remove water after sparging with argon to remove oxygen. NMR solvents were purchased from Cambridge Isotopes Laboratories, Inc. and degassed prior to use. All chemical shifts are reported in units of ppm and referenced to the residual protonated solvent. The 13C NMR assignments are based on decoupled 13C, peak heights for overlapping signals, and DEPT experiments. All spectra were recorded at 23 °C. Conclusions

In summary we have reported a series of Rh(NN'O2=O)(=Cl)(CH3OH) (2a). A 50 mL Schlenk bomb was loaded with RhCl3·(H2O)3 (306 mg, 1.19 mmol) in water (5 mL). To this was added a solution of H2NpyN=O2=O (485 mg, 0.89 mmol, 1 equiv.) in acetone (10 mL). The reaction mixture was heated at 80 °C for 5 min to afford a homogeneous orange solution. After 5 min, NaHCO3 (150 mg, 1.78 mmol) was added to the reaction mixture and the mixture heated at 80 °C for 24 h. After 8 h, the reaction mixture was filtered through Celite, and the volatiles were removed in vacuo. The desired product was crystallized from a minimum amount of CH3OH–CH2Cl2 (1:1) at ~30 °C as light orange micro-crystals (414 mg, mmol, 72%). The NMR spectroscopic data are consistent with trans-isomer in CDCl3; CH3OH. 1H NMR (400 MHz, CD3OD/CDCl3, 1 : 1): 9.41 (d, JHH = 6 Hz, 1H, Py), 7.41 (t, JHH = 7.5 Hz, 1H, Py), 7.00 (t, JHH = 7 Hz, 1H, Py), 6.90 (t, JHH = 3 Hz, 2H, Ar), 6.87 (d, JHH = 3 Hz, 2H, Ar), 6.76 (d, JHH = 8 Hz, 1H, Py), 4.90 (d, JHH = 13 Hz, 2H, CHAr, CHAr'), 4.29 (s, 2H, CH2Py), 3.53 (d, JHH = 13 Hz, 2H, CHAr, CHAr'), 2.12 (s, 18H, t-BuH), 1.19 (s, 18H, t-BuH). 13C[1H] NMR (CD3OD/CDCl3); 157.1, 154.1, 148.7, 141.4, 138.1, 136.9, 125.8, 124.4, 123.95, 123.2, 122.3, 57.4, 56.3, 35.6, 34.7, 32.1, 30.10.

Synthesis of Rh(NNMe2N¢O2=O)(=Cl)(CH3OH) (2b). A 50 mL Schlenk bomb was loaded with RhCl3·(H2O)3 (306 mg, 1.19 mmol) in water (5 mL). To this was added a solution of H2NpyN¢O2=O (485 mg, 0.89 mmol, 1 equiv.) in acetone (10 mL). The reaction mixture was heated at 80 °C for 5 min to afford a homogeneous orange solution. After 5 min, NaHCO3 (150 mg, 1.78 mmol) was added to the reaction mixture and the mixture heated at 80 °C for 24 h. After 8 h, the reaction mixture was filtered through Celite, and the volatiles were removed in vacuo. The desired product was crystallized from a minimum amount of CH3OH–CH2Cl2 (1:1) at ~30 °C as light orange micro-crystals (414 mg, mmol, 72%). The NMR spectroscopic data are consistent with trans-isomer in CDCl3; CH3OH. 1H NMR (400 MHz, CD3OD/CDCl3, 1 : 1): 9.41 (d, JHH = 6 Hz, 1H, Py), 7.41 (t, JHH = 7.5 Hz, 1H, Py), 7.00 (t, JHH = 7 Hz, 1H, Py), 6.90 (t, JHH = 3 Hz, 2H, Ar), 6.87 (d, JHH = 3 Hz, 2H, Ar), 6.76 (d, JHH = 8 Hz, 1H, Py), 4.90 (d, JHH = 13 Hz, 2H, CHAr, CHAr'), 4.29 (s, 2H, CH2Py), 3.53 (d, JHH = 13 Hz, 2H, CHAr, CHAr'), 2.12 (s, 18H, t-BuH), 1.19 (s, 18H, t-BuH). 13C[1H] NMR (CD3OD/CDCl3); 157.1, 154.1, 148.7, 141.4, 138.1, 136.9, 125.8, 124.4, 123.95, 123.2, 122.3, 57.4, 56.3, 35.6, 34.7, 32.1, 30.10.
in water (5 mL). To this was added a solution of \( \text{H}_3\text{N}^{\text{Me}}\text{N}^{\text{O}}\text{O}^{\text{Me}}\) (423 mg, 1.19 mmol, 1 equiv.) in acetone (10 mL). The reaction mixture was heated at 80 °C for 5 min to afford a homogeneous orange solution. After 5 min, NaHCO\(_3\) (200 mg, 2.38 mmol) was added to the reaction mixture and the mixture heated at 80 °C for 6 h. After 6 h, the reaction mixture was filtered through Celite, and the volatiles were removed in vacuo. The desired product was crystallized from a minimum amount of CH\(_3\)OH–CH\(_2\)Cl\(_2\) (1:1) at −30 °C as orange-red micro-crystals (420 mg, mmol, 69%).

The NMR spectroscopic data are consistent with trans-isomer in CDCl\(_3\): CH\(_3\)OH. \(^1\)H NMR (CD\(_3\)OD/CDCl\(_3\), 1:1): 6.78 (d, \( J_{	ext{HH}} = 2 \text{ Hz, Ar} \)), 6.65 (d, \( J_{	ext{HH}} = 2 \text{ Hz, Ar} \)), 5.39 (d, \( J_{	ext{HH}} = 13 \text{ Hz, 2H, CHAr, CHAr'} \)), 3.26 (d, \( J_{	ext{HH}} = 13 \text{ Hz, 2H, CHAr, CHAr'} \)).

The reaction mixture was stirred vigorously for 30 min. After 30 min, the reaction mixture was filtered through Celite, and the volatiles were removed in vacuo. The desired product was crystallized from a minimum amount of CH\(_3\)OH–CH\(_2\)Cl\(_2\) (1:1) at −30 °C as orange-red micro-crystals (360 mg, mmol, 70%). The NMR spectroscopic data are consistent with cis-isomer in CDCl\(_3\): CH\(_3\)OH. \(^1\)H NMR (400 MHz, CD\(_3\)OD/CDCl\(_3\), 1:1): 8.50 (d, \( J_{	ext{HH}} = 5.5 \text{ Hz, 1H, Py} \)), 7.59 (t, \( J_{	ext{HH}} = 6 \text{ Hz, 1H, Py} \)), 7.13 (m, 2H, Py), 6.79 (s, 1H, Ar), 6.70 (s, 1H, Ar), 6.41 (s, 1H, Ar), 6.35 (s, 1H, Ar), 5.53 (d, \( J_{	ext{HH}} = 13 \text{ Hz, 1H, CHAr} \)), 4.98 (d, \( J_{	ext{HH}} = 15 \text{ Hz, 1H, CHAr} \)), 4.19 (d, \( J_{	ext{HH}} = 15 \text{ Hz, 1H, CHPy} \)), 3.77 (d, \( J_{	ext{HH}} = 13 \text{ Hz, 1H, CHPy} \)), 3.53 (d, \( J_{	ext{HH}} = 13 \text{ Hz, 1H, CHAr} \)), 2.75 (d, \( J_{	ext{HH}} = 13 \text{ Hz, 1H, CHAr} \)), 2.33 (s, 3H, Me), 2.15 (s, 3H, Me), 2.00 (s, 3H, Me), 1.85 (s, 3H, Me). \(^{13}\)C\(^{\text{HH}}\) NMR (CD\(_3\)OD/CDCl\(_3\)): 163.0, 149.6, 148.5, 137.5, 137.2, 133.0, 132.0, 129.0, 128.7, 127.7, 123.9, 123.7, 122.1, 121.7, 120.9, 69.7, 66.7, 61.8, 20.50, 20.42, 18.0, 17.1.

Acronyms and abbreviations

ESI-MS Calculated for \( \text{C}_{26}\text{H}_{31}\text{N}_{2}\text{O}_{2}\text{Rh} \) (M – OCH\(_3\)): 555.1519 Found 555.1514.

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Notes and references


7 For more examples see: (a) Zn(NPy(NO\(_3\))\(_2\))\(_2\)\((\text{Bu})\text{Cl}\), (b) Zn(NPy(NO\(_3\))\(_2\))(\text{Cl})\(_2\), (c) Cu(NO\(_3\))\(_2\), (d) Cu(NPy(NO\(_3\))\(_2\))(\text{Cl})\(_2\), (e) Cu(NPy(NO\(_3\))\(_2\))(\text{I})\(_2\). (f) (b) Zn(NPy(NO\(_3\))\(_2\))(\text{Cl})\(_2\), (c) Cu(NO\(_3\))\(_2\), (d) Cu(NPy(NO\(_3\))\(_2\))(\text{Cl})\(_2\), (e) Cu(NPy(NO\(_3\))\(_2\))(\text{I})\(_2\).


